Reprints
Photoacoustic and photoluminescence studies of H⁺ ion-implanted n-GaAs

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The surface of silicon-doped GaAs (100) grown by the vertical Bridgman method has been implanted with H⁺ ions at 30 keV for various doses from 10¹⁴ to 10¹⁷ cm⁻² and studied using photoacoustic and photoluminescence spectroscopy to understand the effects of hydrogen ion implantation on GaAs:Si. The results are compared with Raman measurements. All the measurements confirm the sign change of charge carriers at a dose of 10¹⁵ cm⁻².

1 Introduction

Various studies of ion-implanted n-GaAs, including junction capacitance and carrier removal, have been reported in the literature [1–3], where changes in the crystalline parameters due to H⁺ ion implantation are observed. Dharmarasu et al. [1], from the Raman results of H⁺- and He⁺-implanted crystalline n-GaAs (with carrier concentration <4.2 × 10¹⁷ cm⁻³), reported lattice damage at higher doses. Udayasankar et al. [4] studied 100 keV ion implantation of undoped semi-insulating (100) GaAs single crystals for various ion doses at room temperature and investigated structural properties due to high-dose, low-energy hydrogen ion implantation using X-ray double-crystal diffractometry. They observed for a dose of 10¹⁸ ions cm⁻² a heavily damaged region at the surface but no amorphization for the same dose.

Recrystallization of ion-implanted GaAs was studied by Mcfariane and Hess [5] using photoacoustic spectroscopy. They detected the recrystallization of ion-implanted GaAs by laser annealing. Zegadi et al. [6] analyzed ion-implanted CuInSe₂ single crystals using photoacoustic spectroscopy and observed that the majority carrier concentration changes from n-type to p-type during O⁺ ion implantation.

In impurity semiconductors, the excess charge carriers interact with the lattice leading to a coupling between plasmon and phonons and hence two types of longitudinal optical phonon–plasmon coupled (LOPC) modes appear. The character of these modes depends on the carrier density of the system. The longitudinal optical (LO) and LOPC modes of as-grown and H⁺ ion-implanted (at 30 keV) n-GaAs for various doses (10¹⁷ to 10¹⁷ cm⁻²) were analyzed by Murugan et al. [2] using Raman measurements. The Raman spectra recorded are shown in Fig. 1.

Figure 1 shows the A₁ (LO) phonon mode around 290 cm⁻¹ for all samples and the LOPC mode around 268 cm⁻¹ for unimplanted GaAs. The LOPC mode varies in its characteristics for various doses of H⁺ ions and is absent when the dose is 10¹⁵ cm⁻². For higher doses, the LOPC mode appears at a low frequency and increases with the dose. For low doses, H⁺ and defect complexes passivate the free electrons result-

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ing in a decrease of free carrier concentration and leading to a decrease of the LOPC peak position. This means that the carrier concentration decreases from $2.8 \times 10^{18}$ cm$^{-3}$ to a value less than $4.25 \times 10^{17}$ cm$^{-3}$ (concentration of bulk material) on H$^+$ implantation up to a dose of $10^{15}$ cm$^{-2}$ implying type conversion at this dosage. On increasing the dose, the LOPC mode reappears at $239$ cm$^{-1}$ for a dose of $10^{16}$ cm$^{-2}$ and the LOPC peak position increases with dose implying an increase of free carrier concentration.

Thus Raman studies of these samples reveal a type conversion at a dose of $10^{15}$ cm$^{-2}$. This type conversion is studied in the present paper using photoacoustic and photoluminescence techniques, as these involve direct measure of the energy absorbed by a material as a result of its interaction with the photon beam, and more information can be obtained on optical, elastic and thermal properties.

2 Sample preparation

The samples used in this study were GaAs doped with silicon (~$4 \times 10^{18}$ cm$^{-3}$) that were grown by the vertical Bridgman technique. Boron was doped for impurity hardening and silicon was doped for electrical activity. The n-GaAs samples were obtained in the form of wafers of thickness about $620$ µm and (100) orientation along the plane with a resultant electron carrier concentration of $2.8 \times 10^{18}$ cm$^{-3}$ (GaAs:Si) and carrier mobility of $1.7 \times 10^{3}$ cm$^{2}$ V$^{-1}$ s$^{-1}$. The carrier concentration and mobility were obtained from Hall measurements.

The samples were cut into five pieces of size $2$ mm $\times$ $2$ mm, and implanted at room temperature at $10^{-6}$ mbar pressure with $30$ keV H$^+$ doses of $10^{14}$, $10^{15}$, $10^{16}$ and $10^{17}$ cm$^{-2}$ using a $150$ kV accelerator. The ion penetration depth was estimated to be $266$ nm for $30$ keV H$^+$ in n-GaAs using SRIM-2000 (the details are available in previous papers [2, 3]).

3 Photoacoustic spectroscopy (PAS)

PAS has become an important tool used in the characterization of semiconductors. It is nondestructive and contactless, and is unique in being a direct monitor of nonradiative de-excitation processes and offers the potential for depth profiling analysis. One of the important features of PAS is its potential for detecting subsurface variations in both optical and thermal properties of a sample, including the elastic properties. These advantages have led to the current widespread use of the technique [7–9]. In the case of semiconductors, the photoacoustic signal provides information regarding the carrier transport properties as well as thermal properties.
3.1 PAS experimental set-up

Photoacoustic (PA) measurements were obtained at room temperature using a 450 W xenon lamp (FL-1039, Jobin Yvon, USA), a monochromator (TRIAX series, Jobin Yvon, USA) for different wavelengths, a chopper (PAR chopper) in the frequency range 10 Hz–2 kHz, and a PA cell. A condenser microphone was used as the detector and a lock-in amplifier (7225 PAR, USA) as the display unit for the PA signal.

3.2 PAS measurements

The PA effect is the generation of acoustic waves in a sample resulting from the absorption of photons. When a system becomes amorphous, the phonon spectrum and hence the thermal properties will be affected, as the periodicity is lost. Defects, interstitials and vacancies have important roles in the heat-associated properties. These are the reasons for the importance of PAS in ion-implantation studies.

The PA spectra were obtained by recording the PA signal as a function of the wavelength of the incident beam (350–1100 nm) for constant modulation frequency for as-grown and H⁺ ion-implanted samples for various doses from $10^{14}$ to $10^{17}$ cm⁻². The spectra were normalized using the PA signals from carbon black.

3.3 PAS results and discussion

The PA spectra (Fig. 2) show peaks at photon energies of 1.57, 1.47 and 1.35 eV. The peak at 1.47 eV is the primary peak corresponding to the energy gap of host GaAs (1.42 eV) and the signals at 1.35 and 1.57 eV are the shoulders due to the defects. Since GaAs is a direct band gap semiconductor, the band gap $E_g$ can be estimated from the primary absorption peak of the PA spectrum as

$$\beta h\nu = B(h\nu - E_g)^2$$

where $B$ is a constant, $\beta$ is the absorption coefficient and $E_g$ is the energy gap. Hence from the present PA measurements, 1.47 eV should be the band gap of the GaAs host system. This compares very well with the literature value (1.42 eV). The shoulder peaks at 1.35 and 1.57 eV are closely monitored where the PA intensity starts decreasing from a higher value reaching a minimum at a dose of $10^{15}$ cm⁻² and then increasing. The phase of the PA signal interestingly shows a phase reversal at a dose of $10^{15}$ cm⁻². This is due to the decrease in carrier concentration from $2.8 \times 10^{18}$ cm⁻³ to $<4.25 \times 10^{17}$ cm⁻³ on H⁺ ion implantation. On increasing the dose from $10^{15}$ cm⁻² the PA amplitude (intensity) starts increasing. This implies that the free carrier concentration increases.
It has already been reported that ion implantation of an n-type semiconductor would change it to p-type [10–12]. Narayanan et al. [10] have observed the n- to p-type conversion in CdS film on nitrogen ion implantation using the hot probe method. Narsale et al. [11] carried out tin ion implantation of n-GaAs and reported p-type conductivity of the implanted layer. Zagadi et al. [6] in their analysis of oxygen-implanted CuInSe$_2$ single crystals of 500 µm thickness observed that the majority charge carrier concentration is changed from n-type to p-type after implantation. Murray et al. [12] investigated n-type silicon-doped epitaxial layers of GaAs by measurements of the Hall effect and the strengths of the localized vibrational modes from Si(Ga) donors, Si(As) acceptors, Si(Ga)–Si(As) pairs and Si–X, a complex of silicon with a native defect, were detected. They reported that at higher doping levels Si–X becomes dominant and acts as an acceptor, so reducing the carrier concentration [n].

It has already been discussed in our earlier papers [2, 3] that H$^+$ ion implantation of n-GaAs would change it into p-GaAs for a particular dosage. This ion implantation passivates the free electron at low doses and at fairly high doses it produces defect complexes, which release holes to convert n-type to p-type. Under this condition, the polarity of the charge carriers would reverse with implantation. In fact it is found that the current polarity in a $10^{17}$ cm$^{-2}$ H$^+$-implanted sample is different from that in an unimplanted sample, as measured by the hot probe method. This implies that the type conversion has taken place in this sample on implantation. The phase reversal at a dose of $10^{15}$ cm$^{-2}$ also confirms the type conversion at this dosage.

It is also observed that the overall PA amplitude decreases instead of increases when the dose is increased from $10^{16}$ to $10^{17}$ cm$^{-2}$ (Fig. 2, spectra D and E). This is an indication of the onset of amorphization, which could be the result of increasing defect recombination [3]. This amorphization by implantation with high doses is often considered to be due to overlap of the defect clusters. These variations are shown in Fig. 3, where it is seen that at a dose of $10^{17}$ cm$^{-2}$ there is a type change (from n-type to p-type).

### 4 Photoluminescence (PL)

Although both Raman and PA measurements confirm the type reversal in n-GaAs, further studies, particularly of excitons, should be carried out using PL, because GaAs is a direct band gap semiconductor where excitons will be stable and can transport energy.

PL characterization of silicon-implanted GaAs was studied by Lamberti et al. [13] and Kunert and Brink [14]. In the present work a quantitative study of damage introduced by H$^+$ ion implantation of GaAs is carried out using PL, as such work has not been reported in the literature. The same samples (H$^+$ ion-implanted n-GaAs) as used in the PAS study were used to record the PL spectra.
4.1 PL experimental set-up

The spectrofluorophotometer (Shimadzu RF-5000) consists of a xenon lamp as a source of UV radiation, an excitation monochromator enabling the sample to be excited at different wavelengths, a sample compartment, a fluorescence emission monochromator to observe the radiation emitted at a particular wavelength, and a photodetector to convert the emitted radiation into an electrical signal. In addition slits are present on either side of the monochromator to collimate and limit the range of wavelengths of the exciting and emitted radiation. A cut-off filter is placed between the sample and emission monochromator, which transmits all excitation radiation above a specified wavelength and absorbs completely at lower wavelengths.

4.2 PL measurements

The PL spectra for as-grown samples and samples implanted with 30 keV H\(^+\) ions at different doses (10\(^{14}\), 10\(^{15}\), 10\(^{16}\), 10\(^{17}\) cm\(^{-2}\)), as (100) wafers, were recorded at room temperature. The PL intensity as a function of dose is shown in Fig. 4. Since these are room temperature measurements, the excitons (electron–hole bound pairs) alone are monitored for the different doses.

It is well known that the basic excitonic energies are all below the direct energy gap of the system and so it is natural to expect the excitonic energies only at the proximity of 1.47 eV. If the PL spectra were obtained at low temperatures, the PL peak would give the direct band gap of GaAs (1.47 eV). Since the spectra are recorded at room temperature and as the carrier concentration is greater, the PL peaks corresponding to twice the excitonic energies are concentrated on in the present investigation, as the fundamental excitonic peaks are very weak at room temperature.

The PL spectra consist of the dominant excitonic emission at energies 3.22, 2.86 and 2.36 eV. It is observed (Fig. 4) that all the exciton energies increase with implantation dosage reaching a maximum at 10\(^{15}\) cm\(^{-2}\) and then decrease. This can be understood as follows. When the H\(^+\) ions are implanted in the sample (n-GaAs), excitons are generated as more and more holes are added to majority donors thereby reducing the donor carrier concentration. The generation of more excitons with increasing dose increases the exciton energy. When the dose reaches 10\(^{15}\) cm\(^{-2}\), the exciton energy becomes a maximum implying that the donor carrier concentration decreases from 2.8 \times 10\(^{18}\) cm\(^{-3}\) to a value of less than 5 \times 10\(^{17}\) cm\(^{-3}\).

Under these conditions the n-GaAs changes from n-type to p-type as the holes become dominant. A further increase of dose above 10\(^{15}\) cm\(^{-2}\) decreases the emission intensity as there is no generation of excitons and as there is generation of holes alone. That is, the hole carrier concentration increases with dose above 10\(^{15}\) cm\(^{-2}\).
5 Conclusion

The study of H⁺ ion-implanted n-GaAs samples reveals the sign change of charge carriers. This compares well with the earlier Raman results [2]. All the measurements clearly lead to the conclusion that n-GaAs under H⁺ ion implantation at a dose of \(10^{20}\) cm\(^{-2}\) can change to p-GaAs; i.e. a sign change of the charge carriers.

References

EPR and photoacoustic studies on 30 keV H+ ion-implanted n-GaAs

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Abstract

Electron paramagnetic resonance (EPR) measurements are carried out on the 30 keV H\textsuperscript{+} ion-implanted, Si-doped GaAs (100) for various doses from 10\textsuperscript{14} to 10\textsuperscript{17} cm\textsuperscript{2}. The results are correlated with photoacoustic and photoluminescence measurements. All the measurements confirm the sign change of charge carrier at a dose of 10\textsuperscript{15} cm\textsuperscript{2}.

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1. Introduction

In semiconductors, lattice damages are the most important intrinsic defects which might be introduced during crystal growth or material processing such as ion implantation or etching. Various studies on defects in n-GaAs are reported in literature\cite{1-4} for H\textsuperscript{+} ion implantation. Dharmarasu et al.\cite{1}, from the Raman results of H\textsuperscript{+} and He\textsuperscript{+}-implanted crystalline n-GaAs (with carrier concentration <4.2 \times 10\textsuperscript{17} cm\textsuperscript{-3}) reported lattice damages at higher doses.

Murugan et al.\cite{2} studied H\textsuperscript{+} implantation effects in highly doped n-GaAs by Raman measurements and demonstrated the passivation effect of charge carriers at a dose of 10\textsuperscript{15} cm\textsuperscript{2} from LO phonon–plasmon coupling [LOPC] mode. From LOPC, they have estimated the carrier concentration and the polarity to conclude that there is a type change.

Miksic et al.\cite{5} analyzed the defects in H-implanted silicon by electron paramagnetic resonance (EPR) and showed that heavy dose hydrogen implantation produces vacancy related and silicon clusters. Jones et al.\cite{6} studied ion implantation-induced defects in amorphous hydrogenated carbon by EPR and reported the formation of paramagnetic centers (carbon defect and silicon defect) and change in defect concentration with increasing dose.

Sealy et al.\cite{7} studied defects produced by 3 MeV Au\textsuperscript{+} or 2 MeV Si\textsuperscript{+} ion-implanted silicon by EPR measurements. For implants at 300 K of 5 \times 10\textsuperscript{13}–15 \times 10\textsuperscript{15} Au\textsuperscript{+} cm\textsuperscript{2} and of 3 \times 10\textsuperscript{15} Si\textsuperscript{+} cm\textsuperscript{2} an amorphous layer is produced and D centers are shown by EPR measurements.

In our earlier paper\cite{4}, effect of 30 keV H\textsuperscript{+} ion implantation (doses 10\textsuperscript{14} to 10\textsuperscript{17} cm\textsuperscript{2}) on n-GaAs was studied by photoacoustic (PA) and photoluminescence (PL) measurements. It was observed that there is a type conversion at a dose of 10\textsuperscript{15} cm\textsuperscript{2} from n- to p-type. The photoacoustic (PA) spectra recorded for as-grown and 30 keV H\textsuperscript{+} ion-implanted n-GaAs for various doses (10\textsuperscript{15} to 10\textsuperscript{17} cm\textsuperscript{2}) are shown in Fig. 1.

The PA spectra\cite{4} were recorded as a function of the wavelength of the incident beam (350–1100 nm) for constant modulation frequency for as-grown and 30 keV H\textsuperscript{+} ion-implanted n-GaAs samples for various doses from 10\textsuperscript{14} to 10\textsuperscript{17} cm\textsuperscript{2}. The spectra were normalized using the PA signals from carbon black. The PA spectra (Fig. 1) show peaks at photon energies of 1.57, 1.47 and 1.35 eV. The peak at 1.47 eV is the primary peak corresponding to the...
energy gap of host GaAs (literature value 1.42 eV) and the signals at 1.35 and 1.57 eV are the shoulders due to the defects.

The shoulder peaks at 1.35 and 1.57 eV are closely monitored when the PA intensity starts decreasing from a higher value reaching a minimum at a dose of $10^{15}$ cm$^{-2}$ and then increases. The phase of the PA signal interestingly shows a phase reversal at a dose of $10^{15}$ cm$^{-2}$. This is due to the decrease in carrier concentration from $2.8 \times 10^{18}$ to $4.25 \times 10^{17}$ cm$^{-3}$ (concentration of bulk material) on H$^+$ ion implantation. On increasing the dose from $10^{15}$ cm$^{-2}$ the PA amplitude (intensity) starts increasing. This implies that the free carrier concentration increases.

The variation in shoulder peak energies with dosage is shown in Fig. 2, where it is seen that at a dose of $10^{15}$ cm$^{-2}$ there is a type change (from n- to p-type). The advantage of PA measurements is the monitoring of phase difference between the PA signal and the chopping signal. Here at the dose of $10^{15}$ cm$^{-2}$, a phase change is observed. The same trend is observed by photoluminescence (PL) for these samples. Fig. 3 shows variation of PL intensity of excitons as a function of various doses of H$^+$ ion implantation for different shoulder energies, 3.22, 2.86 and 2.36 eV.

It is observed (Fig. 3) that all the energies (due to the defects) increase with implantation dosage, reaching a maximum at $10^{15}$ cm$^{-2}$ and then decreases. When the H$^+$ ions are implanted in the sample (n-GaAs), more and more holes are added to majority donors thereby reducing the donor carrier concentration. When the dose reaches $10^{15}$ cm$^{-2}$, the shoulder energy becomes a maximum implying that the donor carrier concentration decreases. A further increase of dose above $10^{15}$ cm$^{-2}$ decreases the emission intensity as there is generation of holes alone. That is, the hole carrier concentration increases with dose above $10^{15}$ cm$^{-2}$.

Thus photoacoustic and photoluminescence studies on these samples reveal the type conversion at $10^{15}$ cm$^{-2}$ dosage. When the phase of the PA signal was monitored along with the PA amplitude, it showed phase reversal at a dose of $10^{15}$ cm$^{-2}$. The Hall measurements also confirmed this change, i.e., at lower doses the charge carriers are electrons and at higher doses the charge carriers are holes.

The details of Hall measurements and the polarity of charge carriers are already given in our earlier paper [2] and so not repeated here. This type conversion is studied here by electron paramagnetic resonance (EPR), as this is one of the most powerful methods that can be used to correlate with optical spectra and photoconductive measurements, for the identification of defects. Even if a defect at microscopic level exists, the EPR would immediately identify it, rather than the other methods. By any chance, if any other defect is present than the type conversion, claimed from other experiments, can be easily seen here in EPR. This is the reason why EPR measurements are carried out here on the ion-implanted samples.

2. Sample preparation

Si-doped GaAs (n-GaAs) crystals were synthesized first by Vertical Bridgman technique and then obtained in the form of wafer of thickness about 620 μm in (100) orientation with electron carrier concentration of $2.8 \times 10^{18}$ cm$^{-3}$ (GaAs: Si) and carrier mobility of $1.7 \times 10^3$ cm$^2$/Vs.
The basic characterization of the samples were first carried out. The samples were then cut into five pieces of size 2 mm × 2 mm, and implanted at room temperature at 10⁻⁶ mbar pressure with 30 keV H⁺ doses of 10¹⁴, 10¹⁵, 10¹⁶ and 10¹⁷ cm⁻² by using a 150 kV accelerator (J15 Sames). The ion penetration depth was estimated to be 260 nm for 30 keV H⁺ in n-GaAs using SRIM-2000 (the details are available in previous papers [2,3]). The ion implantations were carried out at Indira Gandhi Centre for Atomic and Research (IGCAR), Kalpakkam, India.

3. Electron paramagnetic resonance (EPR)

It is widely used as a non-destructive technique to study paramagnetic materials containing unpaired electrons. In systems where Jahn–Teller distortion is significant, EPR is the best tool to identify the changes in symmetry. As early as in 1971, Watts et al. [8] had proved that this EPR was very useful in II–VI systems (particularly with the example of ZnSe:P, where there was an ambiguity in the symmetry). So, here n-GaAs (III–V systems) is studied by EPR on ion implantation.

Electron paramagnetic resonance (EPR) measurements were carried out at room temperature using Varian E-112, klystrons for X-band (9.5 GHz) and Q-band (35 GHz) with a maximum microwave power of 200 mW. It has a scan range of 0–20,000 G, modulation amplitude 40 G and gain 10⁵. EPR measurements are thus made at room temperature for as-grown and H⁺ ion-implanted samples of n-GaAs for various ion doses from 10¹⁴ to 10¹⁷ cm⁻² (at SAIF, IIT, Chennai, India). The complete spectra is not given here and only the range of magnetic field, where the impact is significant, is shown.

In general, EPR spectra would reveal three major defects (i) planar vacancies in GaAs (ii) vacancy clusters (Σ) and (iii) dangling bonds in amorphous GaAs (D centers).

Fig. 4 clearly shows that as ion dosage is increased from 10¹⁴ to 10¹⁵ cm⁻², there is a marked change at 10¹⁵ cm⁻² in the shape of the signal (marked as C). When there is no implantation (marked as A in Fig. 4, for as-grown sample n-GaAs), the EPR shows a maximum at 298.21 mT with intensity 21.37 (arb. unit). For 10¹⁴ cm⁻² dosage, there is an increase in the EPR intensity and a right shift is observed along the x-axis (magnetic field axis). This is due to the addition of H⁺ ions, which reduces the carrier concentration (the electrons here) in the sample and hence the spin lattice interaction will be reduced with the decrease in unpaired electron concentration. Consequently the intensity of the EPR line is increased, as seen in the graph. As the dosage is increased, the right shift of the EPR peak is also increased. But at the dosage of 10¹⁶ cm⁻², the EPR peak is moved to the left side, as shown in Fig. 4 (marked as D in the figure). This shift along x-axis is due to change in resonance frequency. This can be understood from Fig. 4. Firstly, the shift was observed towards lower frequency side i.e., 9.4000 to 9.17764 GHz, when the dosage is increased upto 10¹⁵ cm⁻². Further increase in dosage resulted in a shift towards higher frequency side, i.e., 9.17764 to 9.32458 GHz. But while taking the measurements for all these samples, the frequency was set as 9.4 GHz constantly, therefore the shift shown along the B axis is due to the frequency change (normalization of B-axis with respect to frequency is done in the instrument itself, i.e., normalization is inbuilt in the measurements). Every time the frequency was adjusted to 9.4000 GHz when the measurements are done for other dosages). The shifts are attributed due to a decrease in carrier concentration upto 10¹⁵ cm⁻² and increase in carrier concentration from 10¹⁵ to 10¹⁷ cm⁻². And the minimum intensity of EPR at the dosage of 10¹⁵ cm⁻² is attributed to more recombinations that took place at this dosage, i.e., the hole concentration begins to dominate. So there is a change in the EPR signal, as this is basically due to the change in the carrier density (electrons).

The present EPR spectrum shows isotropic resonance line of nearly Lorentzian shape with g = 2.1174 and a line width of ΔB = 22 mT, at 10¹⁵ cm⁻² dosage. (With the observed data, a graph is drawn connecting magnetic field (mT) and EPR intensity and for this a Lorentzian fit was attempted mathematically. Both are shown in the same Fig. 5, which shows the EPR signal nearly Lorentzian). These are associated with the dangling bonds in amorphous GaAs (D centers). Above 10¹⁵ cm⁻² dosage, as the graph goes towards the as-grown system (A), there is a possibility for recrystallization. These EPR results would not straightforward identify whether it is crystallized or not. But with XRD measurements (rocking curve) the recrystallization is identified. The details are available in our earlier paper [3] and so not reported here.

It has already been discussed in our earlier papers [2,4] that H⁺ ion implantation of n-GaAs would change it into p-GaAs for a particular dosage. This ion implantation passivates the free electron at low doses and at fairly high doses it produces defect complexes, which release holes to convert n- to p-type. Under this condition, the polarity of
the charge carriers would reverse with implantation. For low doses the defect complexes passivate the free electrons [2] and hence the free carrier concentration, resulting in the reduction of EPR intensity. For higher doses, implantation-induced paramagnetic defects are very large in number and also, the hole carrier concentration increases with dose after $10^{15}$ cm$^{-2}$. The increase in paramagnetic defects and the hole carrier concentration result in increase of EPR intensity. In fact it is found that the current carriers in a $10^{15}$ cm$^{-2}$ H$^+$-implanted sample is different from that in an unimplanted sample, as measured by the hot probe method. This implies that the type conversion has taken place in this sample on implantation.

Fig. 6 shows the variation of $g$-value for as-grown and H$^+$ ion-implanted samples for various doses from $10^{14}$ to $10^{17}$ cm$^{-2}$. As EPR is quite sensitive to implantation induced defects and any breaking down of the crystalline symmetry, in the present work, the changes in $g$-values are explained on the basis of implantation-induced lattice disorder in n-GaAs. It is already reported in literature [2,3,9] that hydrogen ion implantation in semiconductors interacts with defects to passivate them. Further increase in dosage (above $10^{15}$ cm$^{-2}$) turns the implanted samples toward amorphization [3], resulting in the increased $g$-values. So a buried amorphous layer in this sample cannot be ruled out, i.e., the upper surface of the sample would become crystalline (due to recrystallization process), but there will be amorphous layer buried at an appreciable depth of the material. This is verified now with an X-ray rocking curve [10].

It is already reported in our earlier paper [2] by Raman measurements that Si in GaAs occupies only substitutional site rather than interstitial. This was confirmed by LOPC modes, namely L$^+$ and L$^-$ modes. The A$_1$(LO) and LOPC modes shown by Raman spectrum [2] correspond to substitutional occupancy of Si in GaAs and not the interstitial occupancy. Further, other than these localized modes no other defect mode was shown by the spectrum.

Likewise the EPR spectrum also has not shown any other defect. The disappearance of LOPC mode at $10^{15}$ cm$^{-2}$ is seen as the minimum EPR intensity and this is essentially due to the change in the environment (type of charge carriers) and not due to additional defects.

4. Conclusion

The similarity in the behavior of the PA and PL [4] to that of the EPR signals very clearly demonstrate that there is a change at $10^{15}$ cm$^{-2}$ dosage. The minimum in $g$-value at $10^{15}$ cm$^{-2}$ dosage may be understood as a change in the polarity of charge carriers at this dosage due to change in environment, because EPR has not identified any other defect. In addition to PA, PL, Hall and Raman measurements where the polarity change in the carriers is clearly demonstrated, the present EPR measurements are necessary to endorse the findings that additional defect centers are not the reasons for the change in polarity. So EPR measurements are necessary here, to justify the result already reported, as, when any additional microscopic level defect is present, the EPR will immediately identify it. Here, the previously reported findings on the polarity change of the charge carriers on the H$^+$ ion implantation in GaAs:Si, should be a reliable result, as EPR has not identified any additional defects or Jahn–Teller distortion.

In this way, EPR study is done here to justify the already reported results on the H$^+$ ion implantation in GaAs.

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References


Synthesis and thermal diffusion of nanostructured porous GaAs

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Nanostructured porous GaAs samples were prepared by electrochemical anodic dissolution of GaAs for various current densities and etching periods. The samples are characterized by SEM and photoluminescence (PL) where a blue shift is observed in PL. Thermal properties of this nanostructured GaAs are then studied by photoacoustic (PA) spectroscopy, where one order decrease in thermal conductivity of porous GaAs compared to bulk is observed. Further it is shown that the thermal conductivity of porous GaAs decreases with decrease in size of the particles.

Synthesis and thermal diffusion of nanostructured porous GaAs

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Nanostructured porous GaAs samples were prepared by electrochemical anodic dissolution of GaAs for various current densities and etching periods. The samples are characterized by SEM and photoluminescence (PL) where a blue shift is observed in PL. Thermal properties of this nanostructured GaAs are then studied by photoacoustic (PA) spectroscopy, where one order decrease in thermal conductivity of porous GaAs compared to bulk is observed. Further it is shown that the thermal conductivity of porous GaAs decreases with decrease in size of the particles.

1 Introduction

Porous semiconducting materials having an indirect band gap show visible photoluminescence (PL) emission beyond their band-gap energies [1]. Porous silicon (Si) has thus become a promising material as a visible light emitter and therefore was extensively studied during the recent past. Such works on the compound semiconductors GaP [2-3], SiGe [4] and SiC [5] are now available in literature. Since GaAs is widely used in optoelectronic devices [6], being a direct band gap semiconductor, works on porous GaAs started appearing for various doping densities [7] and electrolytes [8].

Sabataityte et al. [8] prepared porous GaAs by electrochemical etching in a solution of different concentrations and for various etching periods (15 and 30 min) at a constant current density. They investigated the porous layers using SEM, TEM and optical method and showed that the porous layer consists of Ga2O3, As2O3, As2O5 and GaAs and the observed PL spectra consist of “infrared” and “green” spectral structures. The observed short wavelength PL at a range of 590 – 778 nm of the porous layer is explained by the quantum size effect in the GaAs nanocrystals.

Schmuki et al. [9] formed porous GaAs electrochemically on n-type GaAs (100) in a 0.1 M HCl electrolyte and showed that pore sizes are in the micrometer to nanometer range. The size distribution of the pores correlates qualitatively with the intensities and the positions of the PL peaks, whereas variations in the chemical compositions at the surface show no systematic correlations.

Beji et al. [10] obtained typical porous structure with pores diameters ranging from 10 to 50 nm by electrochemical etching of heavily doped p-type GaAs (100) substrate in HF. The room temperature PL of the porous GaAs revealed the presence of two PL bands located at 1.403 eV (885 nm) and 1.877 eV (661 nm) respectively and are attributed to electron-hole recombination in porous GaAs and to the well-known quantum confinement effects in GaAs nanocrystallites.

Eventhough the surface morphology and optical properties of porous GaAs [11] were studied using SEM and TEM, and photoluminescence (PL) respectively by several researchers, only very few works are available on porous GaAs for various current densities and etching times and works on thermal diffusion in porous GaAs...
are also rarely reported. We have already studied H\(^+\) ion implantation in n-GaAs, where observable change in thermal diffusivity with H\(^+\) ion concentration is noticed [12]. As GaAs is strongly replacing all silicon devices, porous study on GaAs becomes important. Therefore here porous GaAs is prepared for various current densities and etching periods to study the thermal properties.

2 Experimental

Preparation of porous GaAs The porous layers on GaAs surface were prepared by electrochemical anodic dissolution of GaAs (100) of 690 \(\mu\)m thickness in 48% hydrofluoric acid, H\(_2\)O and ethanol with platinum electrode as cathode. This GaAs single crystal was grown by Liquid Encapsulated Czochralski (LEC) method which was then cleaved in (100) as wafers of thickness 690 \(\mu\)m. The electrolyte was prepared by mixing HF (48%), H\(_2\)O and ethanol in 1:1:2 ratio. The porous layers on the surface of these samples were prepared for (i) various etching times (5 and 15 min) at a constant current density (30 mA/cm\(^2\)) and (ii) different current densities (30 and 60 mA/cm\(^2\)) at constant etching time of 15 min. For convenience of discussions, these samples are identified as given in table 1 [for example a GaAs etched at a current density of 30 mA/cm\(^2\) (from a constant current source) for etching time 5 min is identified as sample 1 and so on].

<table>
<thead>
<tr>
<th>Sample (GaAs)</th>
<th>Current density (mA/cm(^2))</th>
<th>Etching time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Sample 3</td>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

Characterization of porous GaAs The Scanning electron microscopy (SEM) was used to investigate the etched GaAs samples using Philips XL30 ESEM to confirm the porosity. Only some typical SEM pictures of porous GaAs (sample 2 and 3) are shown here in figure 1. Porosity of 30% and 46% are observed for these samples 2 and 3 respectively.

![SEM picture of (a) Sample 2 (b) Sample 3.](image)

Fig. 1 SEM picture of (a) Sample 2 (b) Sample 3.

The compositions of the porous samples are analyzed with energy dispersive X-rays (EDAX) for the atomic percentage of Ga and As in GaAs which are 46.91 and 53.09 % respectively. The EDAX analysis is compared with the already reported chemical composition of porous GaAs layers [8,11]. Photoluminescence (PL) emission spectra of porous samples 1 to 3 are recorded at room temperature using a spectrofluorophotometer (Shimadzu RF-5000). An estimate of the size of the porous GaAs nanostructure to produce PL peak can be obtained from effective mass theory. Assuming infinite potential barriers, the energy gap \(E_n\) for three-dimensionally confined GaAs should vary as [11],

\[
E_n = E_g + \frac{\hbar^2}{2d^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right),
\]

where \(E_g\) is the energy gap of bulk GaAs, \(d\) is the diameter of the spherical particle, and \(m_e^*\) and \(m_h^*\) are the electron and hole effective masses, respectively. At 300 K, \(E_g = 1.424\) eV, \(m_e^* = 0.063\) and \(m_h^* = 0.53\) [13].

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Here the thermal properties of porous GaAs are studied using photoacoustic (PA) technique, which involves direct measurement of the energy absorbed by a material as a result of its interaction with the photon beam. In the present setup, polychromatic light from a xenon lamp (400W, Jobin Yvon) is mechanically chopped by a mechanical chopper (Model number PAR 650) and focused onto the sample. The sample is placed in a PA cell and a microphone is placed very near to the sample. The PA signal from the sample is fed to a lock-in amplifier (Model Perkin Elmer 7225 DSP) and PA signal amplitude (S) is recorded as a function of chopping frequency (f). The experimental technique and method of calculations are already discussed in our earlier paper [14]. From the slope of the graph (Fig. 4) connecting \( \ln(f) \cdot S \) and \( \sqrt{f} \) (where S is the strength of the PA signal), thermal diffusivity (\( \alpha \)) of the sample is deduced. The thermal diffusivity of porous samples can be calculated using the relation

\[
\frac{\pi l^2}{\alpha} = a \]

where \( \alpha \) - thermal diffusivity, \( a \) - slope of the graph connecting \( \ln(f) \cdot S \) and \( \sqrt{f} \), and \( l \) – thickness of the sample. Thermal conductivity (k) is then calculated using the relation

\[
k = \alpha \rho C_p
\]

in units of W/m-K, where \( \rho \) is the density and \( C_p \) is the specific heat capacity of bulk GaAs.

3 Results and discussion

Photoluminescence  Figure 2 shows spectra of samples (1 and 2) prepared at different etching times and figure 3 shows spectra of samples (2 and 3) prepared at different current densities. The PL peak energies and calculated particle size from eqn. (1) of porous GaAs are shown in table 2. The PL peak energies and calculated particle size from eqn. (1) of porous GaAs are shown in table 2. The Samples 1 and 2 (Table 2) show that the size of particles (~ 8 nm) is not affected; i.e., for a particular current density, the size of the...
particles is almost a constant irrespective of the etching times. It is seen in samples 2 & 3 (Fig. 3) where peak positions are drastically affected and thus the size of the particles (8 to 7 nm) i.e., there is change in peak position and size of the particles with change in current densities.

More sophisticated pseudo-potential calculation [15] of the exciton energies for GaAs nanocrystallites predict a diameter of 5 nm for emission at 663 nm. Thus porous GaAs nanoparticles of the order of 5 nm dimensions are required to observe the visible PL in these samples. This is consistent with the particle size (calculated by eqn. (1)) observed here (Table 2).

It is clear from figures 2 and 3 and table 2, peak positions (corresponding peak energies) in all porous samples are blue shifted from the bulk GaAs whose PL peak is at 1.42 eV (871 nm). For example, the sample 1 (A in Fig. 2) exhibits two PL peaks centered around 670 and 603 nm that are blue shifted from bulk GaAs (871 nm). The PL emission peak of all the samples are in the range of 600-700 nm and that are consistent with PL measurements (~ 590-690 nm) of Sabataityte et al. [8], where the sample was prepared in a solution of HF:C\textsubscript{2}H\textsubscript{5}OH:H\textsubscript{2}O (1:1:1) at a current density of 30 mA/cm\textsuperscript{2}, 15 min. In quantum confinement, the PL peak is shifted to higher energy compared to bulk GaAs in proportion to the degree of electron confinement. This is consistent with the theory of porous Si for increasing porosity [16,17]. Similarly here porous GaAs can be explained as due to quantum confinement for increasing porosity. The porosity observed in samples 2 and 3 (Fig. 1) are 36 and 46 % respectively, i.e., the porosity increases with increase in current density. These different porosities result in different nanometer sized GaAs crystallites around which quantum confinement takes place. Further, more than one observed peak implies that there exits an exciton arising due to the different nanometer sized crystallites and non-uniformity in the porosity. For example the peak positions 601 and 636 nm in sample 3 show that porous GaAs are due to excitons [18]. Similar PL bands (red, green, blue) were observed in other reported PL investigations of electrochemically etched GaAs [8,9,11,19]. Generally excitons would have binding energies in the order of meV. Xu et al. [18] investigated copper-doped zinc oxide nanowires fabricated on copper-coated silicon substrate by sintering technique and reported that the size of the copper-doped zinc oxide nanowires ranges from 30 to 100 nm diameter and obtained a broad and continuous photoluminescence spectra from the ultraviolet to the red region.

On comparing the samples 1 and 2, prepared under different etching times (constant current density), a relative blue shift of 5nm (675 to 670 nm; Fig. 2, A to B) is observed on increasing the etching time. For samples 2 and 3, a relatively high blue shift from 670 to 636 nm (Fig. 3: A to B) is observed on increasing current density. Hence an appreciable blue shift is observed for increasing current density than etching period. The dependence of the PL spectra of porous GaAs as a function of current density studied by Beji et al. [20] reported a yellow band undergoing a blue shift on increasing the current density, which is consistent with our present study (Fig. 3).

**Table 2** PL peak energy (Figs. 1 and 2) and particle size (eqn.(1)) of porous GaAs.

<table>
<thead>
<tr>
<th>Sample (GaAs)</th>
<th>PL peak (nm)</th>
<th>PL peak energy (eV)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>675</td>
<td>1.84</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>607</td>
<td>2.04</td>
<td>6.6</td>
</tr>
<tr>
<td>Sample 2</td>
<td>670</td>
<td>1.85</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>603</td>
<td>2.05</td>
<td>6.5</td>
</tr>
<tr>
<td>Sample 3</td>
<td>636</td>
<td>1.95</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>601</td>
<td>2.06</td>
<td>6.5</td>
</tr>
</tbody>
</table>

**Table 3** Thermal diffusivity and conductivity of porous GaAs at room temperature (error ~ ± 1%).

<table>
<thead>
<tr>
<th>Sample GaAs</th>
<th>Porosity (%)</th>
<th>Particle size (nm)</th>
<th>Thermal diffusivity x10\textsuperscript{-5} (m\textsuperscript{2}/s)</th>
<th>Thermal conductivity Wm\textsuperscript{-1}K\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>28</td>
<td>8.0</td>
<td>0.28</td>
<td>4.9</td>
</tr>
<tr>
<td>Sample 2</td>
<td>30</td>
<td>7.9</td>
<td>0.22</td>
<td>3.8</td>
</tr>
<tr>
<td>Sample 3</td>
<td>46</td>
<td>7.1</td>
<td>0.12</td>
<td>2.1</td>
</tr>
<tr>
<td>Bulk</td>
<td>--</td>
<td>--</td>
<td>4.20</td>
<td>55.0</td>
</tr>
</tbody>
</table>
It is observed that (Table 3) the thermal diffusivities and conductivities of these samples are at least one order less than the bulk GaAs. This decrease is due to the decrease in mean free path resulted from multiple scattering of the phonons. Further the dangling bonds of porous GaAs occurring at the planar GaAs can lead to electron-hole recombinations, for which part of the thermal energy is used and the trapped carrier acquiring a thermal velocity \( \sqrt{\frac{8kT}{\pi m^*}} \) (where \( m^* \), the effective mass of the trapped carrier) from this energy. This also leads to the multiple scattering and hence a reduction in thermal conductivity.

It is seen from Table 3 that there is a little variation in thermal conductivity between samples 1 and 2 (prepared at etching periods of 15 and 30 min at constant current density) as there is no appreciable variation in porosity (28 and 30 %) and particle size (\( \sim 8 \) nm). But, an appreciable change in the thermal conductivity is observed for samples 2 and 3 which are prepared at different current densities. For example, when the current density is increased from 30 mA/cm\(^2\) to 60 mA/cm\(^2\) (at constant etching period of 15 min), the thermal conductivity decreases from 3.8 to 2.1 W/m\( \cdot \)K (Sample 2 and 3). This can be understood in terms of porosity and particle size. It is observed from Table 2, that there is an appreciable change in particle size from 8.0 to 7.1 nm with increase in current density as a result of increase in porosity (Fig. 1) from 30 to 46 % for samples 2 and 3 respectively. This decrease in particle size results in reduction in thermal conductivity of the porous samples. Thus the reduction in thermal conductivity is because of decrease in phonon mean free path due to phonon confinement around nano-crystallites formed due to the decrease in particle size and increase in porosity. That is, the decrease in thermal conductivity with etching parameter (current density) is due to the decrease in mean free path due to the phonon confinement in crystallite; when the phonon mean free path is less than the crystallite size, phonons are confined and so the thermal conductivity is reduced.

Qing Shen et al. [21] reported the dependence of thermal conductivity of porous silicon (PS) on porosity by photocoustic technique and showed that the thermal conductivity of PS films decreases with increase in porosity. Jie Zou et al. [22] investigated phonon heat conduction in a semiconductor nanowire and reported that phonon confinement and boundary scattering lead to a significant decrease of the lattice thermal conductivity, which is consistent with our present results.

4 Conclusions

Single crystalline GaAs is grown in (100) orientation by Liquid Encapsulated Czochralski (LEC) method and porous layers are prepared on this for different current densities and etching periods. The samples are then characterized by SEM, PL and EDAX analysis. An appreciable change in porosity and particle size was observed with current density whereas little variation is observed with etching time. The calculated particle size of all the above samples show that they are in nanometer (nm) and so observed blue shift in PL peak. Thermal conductivity by photocoustic measurements showed one order decrease in thermal conductivity of porous GaAs compared to bulk. Further it is shown that the thermal conductivity of porous GaAs decreases with decrease in size of the particle and is discussed in terms of phonon confinement which is due to the decrease in phonon mean free path around nano-crystallites. That is, when the phonon mean free path is less than the crystallite size, phonons are confined and so the thermal conductivity is reduced. Since works on thermal properties of porous GaAs are very sparse, the present values add new data to literature, as this material (band gap widening and lower thermal conductivity) is suitable for optoelectronic devices.

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References